Example 1

Solubility Study of Polymer Resin

A composition comprising carbon dioxide, poly(FOMA-r-TBM), and a photoacid generator is exposed to radiation. The following illustrates the reaction which occurs resulting in the formation of poly(FOMA-r-MAA):

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The polymer contains 33 mol percent of TBA. Poly (FOMA-r-TBM) is determined to be soluble at 1500 psi as measured by a room temperature cloud point measurement. Poly (FOMA-r-MAA) is determined to be insoluble at 5000 psi as measured by the cloud point measurement. Using 33 mol percent of TBA provides solubility contrast for spin coating, and development with carbon dioxide.

Example 2

Solubility Study of Polymer Resin

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The procedure according to Example 1 is followed except that 20 mol percent of TBM is used. Poly (FOMA-r-TBM) is determined to be soluble at 1350 psi as measured by a room temperature cloud point measurement. Poly (FOMA-r-MAA) is determined to be insoluble at 5000 psi as measured by the

^{1 4} weight percent CO2

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cloud point measurement. Using 20 mol percent of TBA provides solubility contrast for spin coating, and development with carbon dioxide.

Example 2

Solubility Study of Polymer Resin

The procedure according to Example 1 is followed except that 12 mol percent of TBM is used. Poly (FOMA-r-TBM) is determined to be soluble at 1260 psi as measured by a room temperature cloud point measurement. Poly (FOMA-r-MAA) is determined to be soluble at 3000 psi as measured by the cloud point measurement. Using 12 mol percent of TBA provides solubility contrast for spin coating, development, and stripping with carbon dioxide.

This invention encompasses methods of forming patterned resist layers on a variety of substrates (including but not limited to silicon, ceramics, polymer, gallium arsenide, silicon carbide, glass, polycarbonate, quartz, poly(tetrafluoroethylene), gold). These resist layers include at least one monomer, a polymer, a photoactive compound and carbon dioxide as a casting solvent and/or processing solvent.

Examples of methods to cast are spin coating (e.g., as described in U.S. Patent No. 6,001,418, the disclosure of which is incorporated herein by reference in its entirety), free-meniscus coating (e.g., as described in U.S. Patent No. 6,083,565, the disclosure of which is incorporated herein by reference in its entirety), dip coating, spray coating, and self-assembling monolayers including those described hereinabove.

The materials for coatings include, without limitation, precursors, monomers, polymers, and oligomers such that these materials are soluble in CO_2 , as well as CO_2 in combination with inert gases, co-solvents, and CO_2 -soluble surfactants, as well as other gases that can control viscosity, surface tension, and density of the liquid phase. " CO_2 -philic" include those set forth herein as well as, without limitation, perfluoroalkyl substituted norbornene monomers, dinorbornene, and alicyclic monomers that increase etch resistance and Tg of the polymers. Siloxane polymers may be employed, as well as coating materials.

Other examples of resist materials are fluorinated resists include those described in WO 00/67072, the disclosure of which is incorporated herein by reference in its entirety. These resists may include, as an example appropriate components, e.g., photoactive components including, without limitation, those described herein as deemed necessary.

In certain embodiments, resists comprise a fluorine-containing polymer comprising a repeat unit derived from at least one ethylenically unsaturated compound containing a fluoroalcohol functional group having the structure:

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-C (R_f) (R_f) OH

wherein R_f and R_f are the same or different fluoroalkyl groups of from 1 to about 10 carbon atoms or taken together are $(CF_2)_n$ wherein n is 2 to 10. The fluorine-containing polymer has an absorption coefficient of less than 4.0 pm~l at a wavelength of 157 nm.

In another embodiment, the resist comprises a fluorine-containing copolymer comprising a repeat unit derived from at least one ethylenically unsaturated compound characterized in that at least one ethylenically unsaturated compound is cyclic or polycyclic, at least one ethylenically unsaturated compound contains at least one fluorine atom covalently attached to an ethylenically unsaturated carbon atom, and at least one ethylenically unsaturated compound is comprised of a fluoroalcohol functional group having the structure:

-C (R_f) (R_f')OH

wherein R_f and R_f' are the same or different fluoroalkyl groups of from 1 to about 10 carbon atoms or taken together are $(CF_2)_n$ wherein n is 2 to 10. The fluorine-containing copolymer may contains sufficient functionality to render the photoresist developable so as to produce a relief image upon imagewise exposure to ultraviolet radiation having wavelength of < 365 nm.